

APPENDIX A

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1142 SUPEROXIDES

such as ethylene, ethane, and carbon dioxide has been measured primarily using dynamic experimental techniques to develop a pressure-temperature-composition (P-T-x) data base for modeling SFE. Compared to conventional gas chromatography, SFC offers lower separation temperatures for thermally labile substances and the alternative of pressure programming to achieve fractionation instead of temperature programming.

Ternary systems. A near-supercritical solvent can be used to modify the mutual miscibility of a binary mixture.

Ternary systems near the critical point of the supercritical solvent may display regions of three-phase behavior, which are analogous to the binary case. For the system ethylene-methyl ethyl ketone-water, small loadings of ethylene below its critical pressure greatly reduces the mutual miscibility, yielding a selectivity of 705.

The combination of a supercritical as well as a liquid solvent provides flexibility in utilizing the advantages of both types of solvents. In a system of two solids in equilibrium with a supercritical fluid, the solubility of a given solid may be significantly enhanced when the second solid also dissolves in the fluid. These benefits resulting from supercritical solvents with or without entrainers should lead to a wide variety of new separation processes.

Theory of Supercritical-Fluid Phase Behavior

Quantitative correlation and, to a lesser degree, prediction of supercritical-solution phase behavior are beginning to emerge, based on recent advancements made in high pressure solution thermodynamics, using computers. The development of thermodynamic models presents two problems: these mixtures are often highly asymmetric, in terms of the size and energy differences between the components reflected, eg, in the critical properties; and the isothermal compressibility of the fluid is ca 1000 times that of a triple-point liquid. Dissolution of a solid in the highly compressible fluid leads to strong attraction that causes the mixture to contract with very large negative values of the partial molar volume of the solute.

Thermodynamic models for SFE are based on the principle that the fugacities, f_i , of component i are equal for all phases at equilibrium at constant temperature and pressure. In the supercritical-fluid phase, the fugacity can be represented by an expression for an expanded liquid or a dense gas.

Most recent investigators have chosen the dense-gas approach utilizing two or three parameter cubic equations of state that are suitable for compressible mixtures. These models are used to calculate the fugacity coefficient of the solute, which is typically on the order of 10^{-4} , and is the primary contributor to the enhancement factor.

Environmental Considerations

The safety features of carbon dioxide make it an attractive solvent for the food and pharmaceutical industries. Generally, SFE does not leave residues in the product.

As the ASME Code is limited to 20.7 MPa (3000 psi), most of the designs for SFE are restricted below this pressure, if possible, to avoid further regulations. At these pressures, the stored energy is much larger for highly compressible supercritical fluids compared with incompressible liquids.

Applications

Carbon dioxide can be used to extract thermally labile food components at near-ambient temperatures. A process for the removal of caffeine from coffee beans using supercritical carbon dioxide was patented in the United States in 1974. One process uses water to wash the caffeine from this mixture, and another uses activated carbon to adsorb the caffeine. The third and most simple method involves charging a vessel containing the beans and activated carbon to supercritical conditions to cause the caffeine to migrate to the fluid phase where it is subsequently adsorbed by the carbon. Carbon dioxide is used to extract α -acids from hops. The USDA has been testing supercritical carbon dioxide for extraction of oils, particularly triglycerides, from soybean flake and corn germ. Supercritical fluids are used for the extraction of flavors and fragrances in natural products (see Coffee; Fats and fatty oils; Flavors and spices; Perfumes).

The energy costs for distillation or liquid solvent extraction have increased tenfold during the last decade; therefore, the less-energy-intensive SFE can be attractive if the capital costs for high pressure equipment are not prohibitive. Several feedstocks, including atmospheric and vacuum-distillation residues, were converted to cat-cracker feed and lubricating-oil stocks using supercritical pentane. Supercritical-fluid extraction can be used to fractionate low-vapor-pressure oils.

Supercritical fluids are utilized in coal processing in the critical solvent deashing process. In the coal-SFE process, a mixture of bicyclic aromatic/naphthenic hydrocarbons is used to dissolve coal and to stabilize the intermediate products from the thermal decomposition.

Supercritical-fluid extraction has been proposed to derive alternative sources of fuel from tar sands (qv), lignite (qv), wood (qv), and oil shale (qv).

Other applications involve the separation of chemicals from aqueous solutions, separations of specialty chemicals, environmental control of crystal growth, solids settling, and polymer processing.

Although a number of companies are known to be developing supercritical fractionation and processing methods for polymers, the specific applications are proprietary.

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SUPEROXIDES. See Peroxides and peroxy compounds.

SUPERPHOSPHATE. See Fertilizers.

SURFACTANTS AND DETERGIVE SYSTEMS

The term surfactant is a contraction of the longer, more awkward term surface-active agent. Coined in 1950, surfactant has become usually accepted to describe organic substances with certain characteristic features in structure and properties. The term detergent is often interchangeably with surfactant. As a designation for a substance capable of cleaning, detergent can also encompass inorganic substances; these do in fact perform a cleaning chore. More often, detergent is a combination of surfactants with other substances, organic or inorganic, formulated to enhance functional performance, specifically cleaning that of the surfactant alone. It is so used in this article.

Surfactants are characterized by the following features:

Amphipathic structure. Surfactant molecules are composed of two parts of opposing solubility tendencies, typically an oil-soluble hydrocarbon chain and a water-soluble ionic or polar group.

Solubility. A surfactant is soluble in at least one phase of a system.

Adsorption at interfaces. At equilibrium, the concentration of surfactant solute at a phase interface is greater than its concentration in the bulk of the solution.

Orientation at interfaces. Surfactant molecules and ions form ordered monolayers at phase interfaces.

Micelle formation. Surfactants form aggregates of molecules called micelles when the concentration of the surfactant solute in the bulk of the solution exceeds a limiting value, the so-called critical micelle concentration (CMC), which is a fundamental characteristic of the solute-solvent system.

Functional properties. Surfactant solutions exhibit combinations of cleaning (detergency), foaming, wetting, emulsifying, solubilizing, and dispersing properties.

Surfactants classification depends on the charge of the surface-active moiety, usually the larger part of the molecule. In anionic surfactants, this moiety carries a negative charge. In cationic surfactants, the charge is positive. In nonionic surfactants there is no charge on the molecule. Finally, in amphoteric surfactants, solubilization is provided by the presence of positive and negative charges in the molecule.

In general, the hydrophobic group consists of a hydrocarbon chain containing ca 10–20 carbon atoms. The chain may be interrupted by oxygen atoms, a benzene ring, double bonds, and amide, ester, and other functional groups. A propylene oxide hydrophobe can be considered as a hydrocarbon chain in which every third methylene group is replaced by an oxygen atom. In some cases, the chain may carry substituents, most often halogens. Siloxane chains have also served as the hydrophobic in some surfactants developed in recent years.

Hydrophilic, solubilizing groups for anionic surfactants include carboxylates, sulfonates, sulfates, and phosphates. Cationics are solubilized by amine and ammonium groups. Ethylene oxide chains and hydroxyl groups are the solubilizing groups in nonionic surfactants. Amphoteric surfactants are solubilized by combinations of anionic and cationic solubilizing groups.

The molecular weight of surfactants ranges from a low of ca 200 to a high in the thousands for polymeric structures.

In the application of surfactants, physical and use properties, precisely specified rather than chemical homogeneity are of primary concern.

Anionic Surfactants

Carboxylate, sulfonate, sulfate, and phosphate are the polar, solubilizing groups found in anionic surfactants. In dilute solutions of soft water, these groups are combined with a C_{12} -chain hydrophobe for best surfactant properties. In neutral or acidic media, or in the presence of heavy metal salts, the carboxylate group loses most of its solubilizing power.

Of the cations (counterions) associated with polar groups, sodium and potassium impart water solubility, whereas calcium, barium, and magnesium promote oil solubility. Ammonium and substituted ammonium ions provide both water and oil solubility. Triethanolammonium is a commercially important example. Salts of these ions are often used in emulsification.

Higher ionic strength of the medium depressed surfactant solubility. To compensate for the loss of solubility, shorter hydrophobes are used for application in high ionic-strength media.

Carboxylates. Soaps represent most of the commercial carboxylates. The general structure of soap is $RCOO^-M^+$, where R is a straight hydrocarbon chain in the C_8 – C_{22} range and M^+ is a metal or ammonium ion. Interruption of the chain by amino or amido linkages leads to other structures, which account for the small volumes of the remaining commercial carboxylates.

Large volumes of soap are used in industrial applications as gelling agents for kerosene and paint driers and as surfactants in emulsion polymerization (see Soap; Driers and metallic soaps; Emulsions). Soap usage in consumer products is principally in person washing products, ie, soap bars.

Carboxylates include polyalkoxycarboxylates and *N*-acylsarcosinates.

Acylated protein hydrolysates. These surfactants are prepared by acylation of protein hydrolysates with fatty acids or acid chlorides. The hydrolysates are variable in composition, depending on the degree of hydrolysis. Collagen from leather processing is a common protein source. Acylated protein hydrolysates are mild surfactants recommended for personal-care products (see also Cosmetics).

Sulfonates. The sulfonate group, $-SO_3M$, attached to an alkyl, aryl, or alkylaryl hydrophobe, is a highly effective solubilizing group. Sulfonic acids are strong acids and their salts are relatively unaffected by pH. They are stable to oxidation and, because of the strength of the C–S bond, also to hydrolysis. They interact moderately with the hardness ions Ca^{2+} and Mg^{2+} , significantly less so than carboxylates. Modification of the hydrophobe in sulfonate surfactants, by introduction of double bonds or ester or amide groups into the hydrocarbon chain or as

substituents, gives surfactants that offer specific performance advantages.

Because the introduction of the SO_3H function is inherently inexpensive, eg, by oleum, SO_3 , SO_2 , Cl_2 , or $NaHSO_3$, sulfonates are heavily represented among the high-volume surfactants (see also Sulfonation and sulfation).

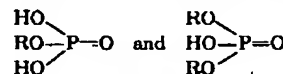
Sulfonates include alkylbenzenesulfonates; alkylarenesulfonates, short-chain lignosulfates; naphthalenesulfonates; α -olefinsulfonates; petroleum sulfonates; and sulfonates with ester, amide, or ether linkages.

Sulfates and sulfated products. The sulfate group, $-OSO_3M$, which can be viewed as the sulfuric acid half-ester of an alcohol, is more hydrophilic than the sulfonate group because of the presence of an additional oxygen atom. Attachment of the sulfate group to a carbon atom of the hydrophobe through the C–O–S linkage limits hydrolytic stability, particularly under acidic conditions.

Usage of sulfated alcohols and sulfated alcohol ethoxylates has expanded dramatically during the last decade as the detergent industry reformulated consumer products to improve biodegradability and lower phosphate content.

Other sulfates include alkylphenols, (ethoxylated and sulfated); sulfated acid, amides and esters and sulfated natural oils and fats.

Phosphate esters. The mono- and diesters of orthophosphoric acid



and their salts are useful surfactants.

In contrast to sulfonates and sulfates, the resistance of alkyl phosphate esters to acids and hard water is poor. Calcium and magnesium salts are insoluble. In the acidic form, the esters show limited water solubility; the alkali metal salts are more soluble. The surface activity of phosphate esters is good, although in general it is somewhat lower than that of the corresponding phosphorus-free precursors. Thus, a phosphated nonylphenol ethoxylated with 9 mol of ethylene oxide is less effective as a detergent in hard water than its nonionic precursor. At higher temperatures, however, the phosphate surfactant is significantly more effective.

Because of their high cost and the limitations noted above, phosphate surfactants find application as specialty surfactants in situations where such limitations are of no concern. As specialty surfactants, phosphate esters and their salts are remarkably versatile. Applications include emulsion polymerization of vinyl acetate and acrylates; drycleaning compositions where solubility in hydrocarbon solvents is a particular advantage; textile mill processing where stability and emulsifying power for oil and wax under highly alkaline conditions is called for; and industrial cleaning compositions where tolerance for high concentrations of electrolyte and alkalinity is required. In addition, phosphate surfactants are used as corrosion inhibitors, in pesticide formulations, in papermaking, and as wetting and dispersing agents in drilling-mud fluids.

Nonionic Surfactants

Unlike anionic or cationic surfactants, nonionic surfactants carry no discrete charge when dissolved in aqueous media. Hydrophilicity in nonionic surfactants is provided by hydrogen bonding with water molecules. Oxygen atoms and hydroxyl groups readily form strong hydrogen bonds, whereas ester and amide groups form hydrogen bonds less readily. Hydrogen bonding provides solubilization in neutral and alkaline media. In a strongly acidic environment, oxygen atoms are protonated, providing a quasi-cationic character. Each oxygen atom makes a small contribution to water solubility. More than a single oxygen atom is therefore needed to solubilize a nonionic surfactant in water. Nonionic surfactants are compatible with ionic and amphoteric surfactants. Since a polyoxyethylene group can easily be introduced by the reaction of ethylene oxide with any organic molecule containing an active hydrogen atom, a wide variety of structures can be solubilized by ethoxylation.

Polyoxyethylene surfactants (ethoxylates). Ethoxylates are moderate foamers and do not respond to conventional foam boosters. Foaming shows a maximum as a function of ethylene oxide content. Low foaming